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Theoretical approaches on the corrosion inhibition property of some important medicinal compounds against industrial imperative metals via computational methods

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Abstract

Even though some cited work carried out on some medicinal compounds as corrosion inhibitors on metals in any corrosive ions, still work is needed on this field in order to take research work to industrial level applications. Hence, in this work, the theoretical work is performed on the Ibuprofen, Aspirin, Paracetamol, Ranitidine, Acetaminophen, Warfarin, Naproxen, Phenazone, Propyphenazone and Caffeine compounds to examine their corrosion inhibition property. The theoretical results obtained from this investigation give a strong platform to experimental investigation. The purpose of current study is to give the mechanism of metal corrosion inhibition by atomic level. For this, theoretical tool, i.e. quantum calculations were adopted. The different parameters such as, E_{LUMO}, E_{HOMO}, dipole moment (μ), global hardness (η), (energy gap (ΔE), absolute electro negativity (χ), from the medicinal molecule was calculated. Results of quantum studies show that, electron rich species in the medicinal substances participate in the phenomena of adsorption process.

Keywords: Corrosion inhibition, quantum calculations, adsorption process, medicinal compound, metals.

Introduction

Chemical, engineering, sugar and pharmaceutical industry faces severe economic problems in the picking, descaling and etching process at the time of shutdown of the plants. The scale deposited on the surface of the metals of evaporators, boilers and heat exchangers. This scale deposited reduces the heat transfer, which reduces the efficiency of equipments[1-5]. Hence, picking, descaling and etching process is vital for the appropriate operation of these plants. For this purpose, strong acid and alkali solutions are used to minimize the disintegration process. Therefore, it is required to minimize the disintegration process. Improvement of methods to control metal corrosion is a tough challenge to scholars working in this area. Hence, finding the way for the controlling the metal corrosion rate has become the blistering topic of recent research.

The phenomena of dissolution or disintegration of the metals in hostile fluid systems can be prevented by the anodic protection, cathodic protection, inhibitors, coatings, abrasive blasting, enameling, design modifications, painting, lubrication, Hot-Dip Galvanization and painting. Among these, inhibitors became the viable, effective and practical method for the combating metal corrosion problems. This decreases the metal consumption and increases the lifespan of industrial important metals[6-10].

Inhibitor is the chemical substance when added to the corrosive liquids in small amounts strongly blocks the metal disintegration process by adsorption mechanism. Inhibitor contains N, S, O and P elements with polar groups. These are the important centers for the generation of the adsorption process. The existing synthetic corrosion inhibitors are noxious and expensive. Hence, there is a necessity to build up the ecological corrosion inhibitors. Previous research report shows that, medicinal compounds are substituted to the synthetic organic species. Even though several medicinal compounds are reported as non toxic corrosion inhibitors for industrial important metals in any media, further research is required to solve the industrial problems. In this regards, development of medicinal corrosion inhibitor compounds alternative to the toxic synthetic species is an elemental field of study. Quantum chemical calculations are one of the important computational methods in metal corrosion inhibition studies[11-13]. By Quantum chemical calculations, it is possible to portray the molecular structure, inhibition mechanism and interactions of the medicinal compounds. Hence, in present study, we selected Ibuprofen, Aspirin, Paracetamol, Ranitidine, Acetaminophen, warfarin, Naproxen, Phenazone, Propyphenazone and Caffeine drugs. The theoretical calculations by quantum chemical method give a solid platform to the experimental methods to solve the metal dissolution problems in industrial level units. In this regard, the present aim was to examine the effect of medicinal compound structure on the protection efficiencies and to obtain information about the corrosion inhibition mechanism by using quantum chemical calculations (computational analysis).The present investigation definitely useful to the exploration of medicinal compounds as new non toxic corrosion inhibitors on different metals in any corrosive media.

Materials and methods

Molecular structures: Structures of Ibuprofen, Aspirin, Paracetamol, Ranitidine, Acetaminophen, warfarin, Naproxen, Phenazone, Propylphenazone and Caffeine were acquired from the literature for quantum parameter analysis. For quantum chemical parameters investigation the structure are taken in "mol" format.

Software and Quantum chemical calculation: Quantum chemical methods have been demonstrated as prevailing tool for examining inhibition of industrial important electrodes (metals) in various corrosive environments. The Quantum chemical parameters such as energy of lowest unoccupied molecular orbital (E_{LUMO}), energy of highest occupied molecular orbital (E_{HOMO}), ionization potential (I), chemical potential (μ), electron affinity (A), Chemical softness or electron polarizability (σ,) chemical hardness (η), electrophilicity index (ω) and electro negativity (χ) were determine from the ArgusLab software (advance version).

E_{HOMO} and E_{LUMO} values are directly obtained from the ArgusLab software. Ionization potential (I) can be calculated by using following relation,

$$I = -E_{HOMO}$$

The values of electron affinity (A) obtained with the help of E_{LUMO} values as follows,

$$A = -E_{LUMO}$$

Electronegativity (χ) and Global hardness (η) can be evaluated as follows respectively,

Electronegativity (χ)= $\frac{I+A}{2}$

Chemical hardness (η)= $\frac{I-A}{2}$

Electron polarizability or chemical softness (σ) is calculated from the below equation,

$$\sigma = \frac{1}{\eta}$$

Chemical potential (μ) is calculated from the below mathematical equation,

$$\mu = -\chi$$

Electrophilicity index (ω) is obtained from below equation,

$$\omega = \frac{\mu^2}{2\eta}$$

The detailed information about the adsorption elements and double bonds present in the medicinal compounds that is responsible for the adsorption process (which prevents the dissolution reaction) is shown in the Table-1.

From Table-1, it is clearly observed that, Ranitidine is the only the medicinal compound which contains S atoms. Paracetamol, Ranitidine, Acetaminophen, Phenazone, Propylphenazone and Caffeine medicinal compounds contain N atoms. All the examined compounds contain O atoms. Among the examined compounds, Ibuprofen, Aspirin, Paracetamol, Acetaminophen, warfarin and Naproxen possessing hydroxyl (OH) groups. All ten medicinal compounds contain double bonds. Generally, we know that, any compounds show corrosion inhibition property if it contains N, S, P and O atoms and double bonds in their moieties. Hence, all ten selected compounds in our investigation obey the general model of corrosion inhibitors.

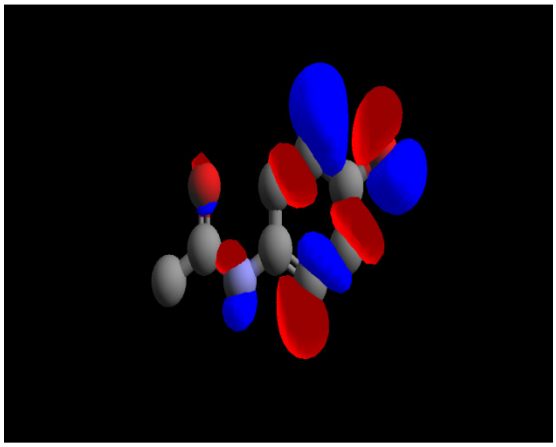
Table-1: Detailed information about the medicinal compounds.

Compound name	Number of "S" atoms present	Number of "N" atoms present	Number of "O" atoms present	Number of "OH" groups present	Number of double bonds present
Ibuprofen	-	-	1	1	4
Aspirin	-	-	4	1	5
Paracetamol	-	1	2	1	4
Ranitidine	1	4	3	-	4
Acetaminophen	-	1	2	1	4
warfarin	-	-	4	1	9
Naproxen	-	-	3	1	6
Phenazone	-	2	1	-	5
Propylphenazone	-	2	1	-	5
Caffeine	-	4	2	-	4

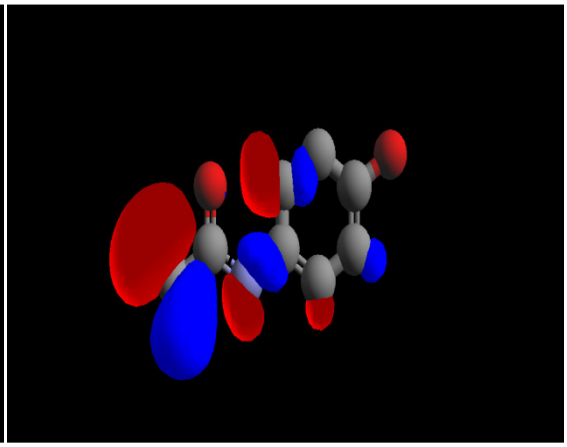
Results and discussion

The HOMO and LUMO orbital's of Acetaminophen, Aspirin, Caffeine, Ibuprofen, Naproxen, Paracetamol, Phenazone, Propylphenazone, Ranitidine and Warfarin were shown Figure-1.

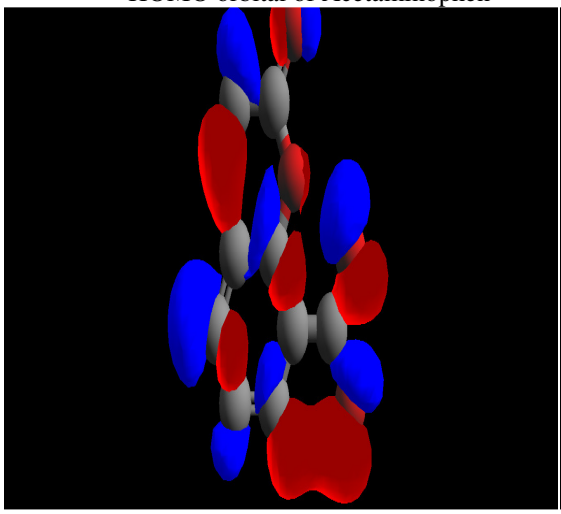
The investigation of E_{LUMO} and E_{HOMO} are vital in order to discover the electronic properties of the medicinal species theoretically. The negative and positive phases of the orbital are represented by two colors, the red color indicates the decrease in the electron density and blue color shows the increase in the electron density.



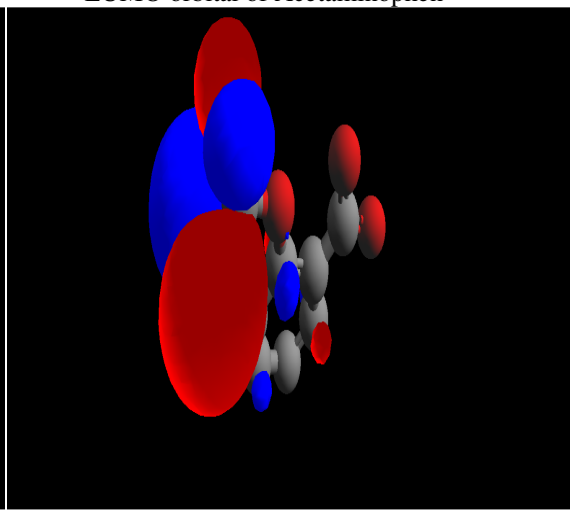
HOMO orbital of Acetaminophen



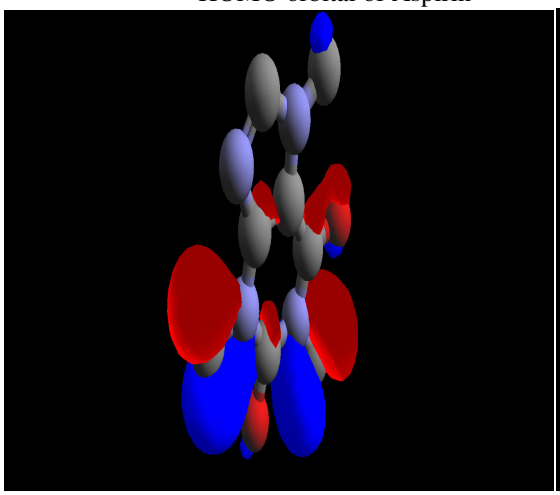
LUMO orbital of Acetaminophen



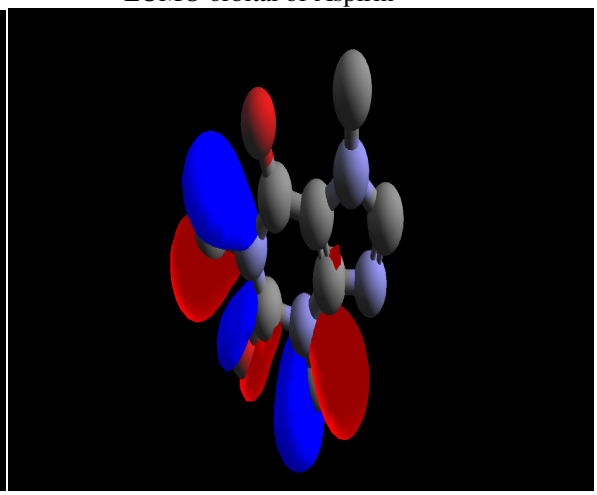
HOMO orbital of Aspirin



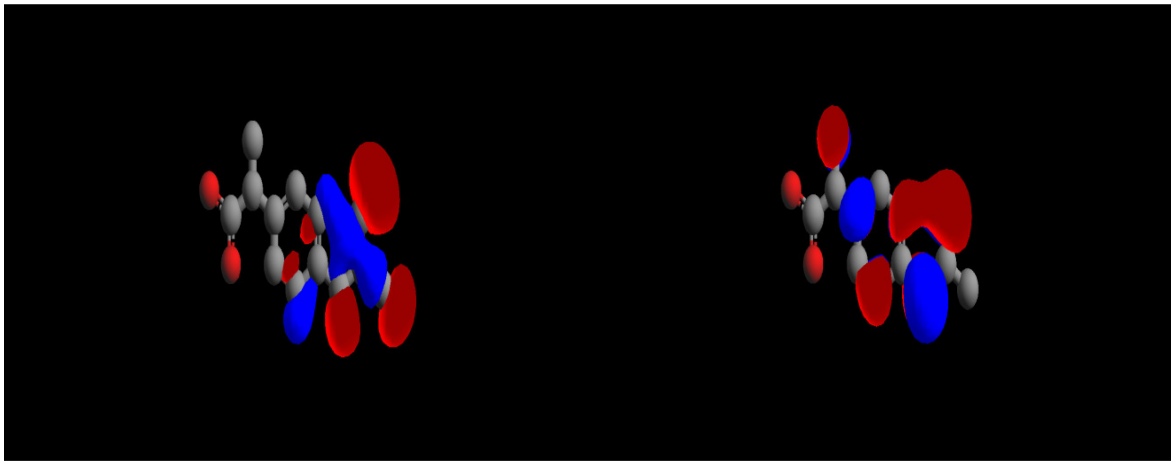
LUMO orbital of Aspirin



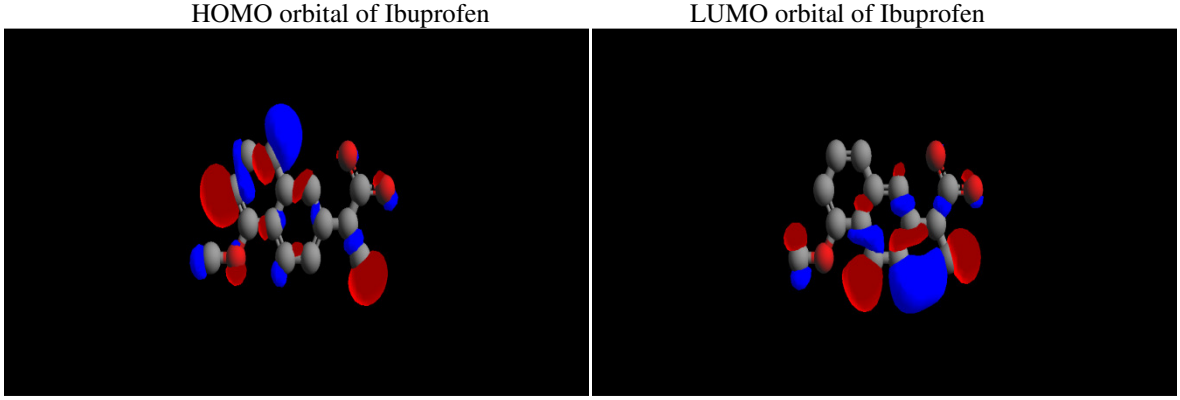
HOMO orbital of Caffeine



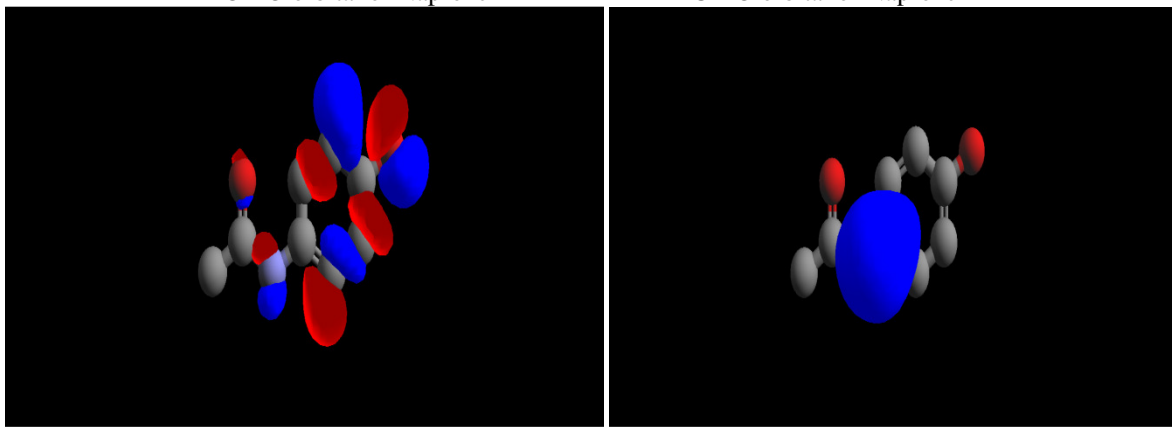
LUMO orbital of Caffeine



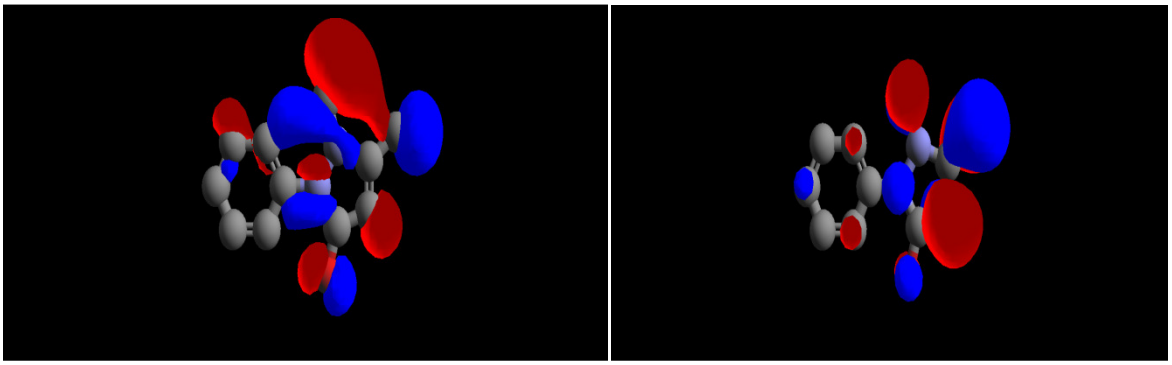
HOMO orbital of Ibuprofen LUMO orbital of Ibuprofen



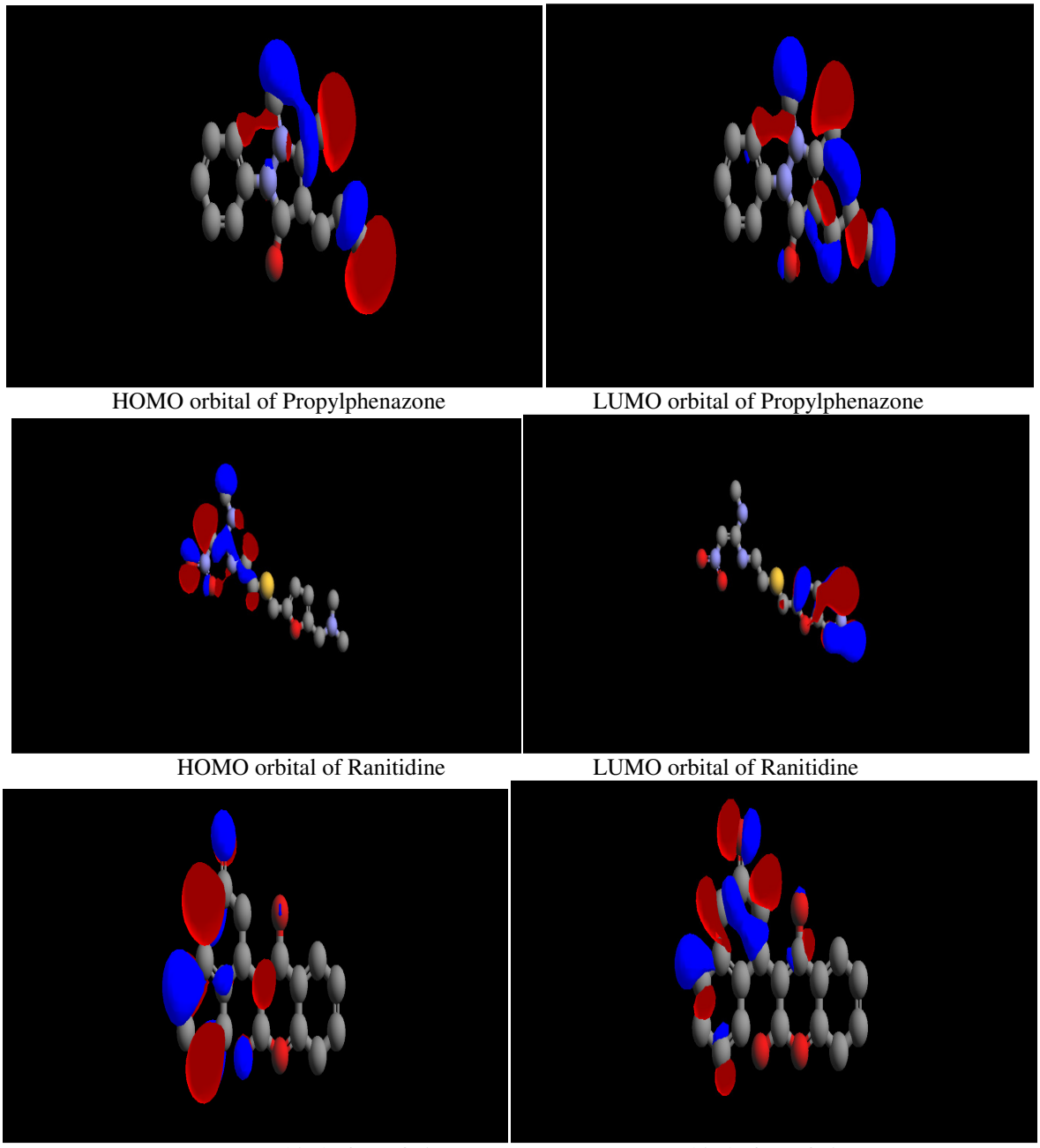
HOMO orbital of Naproxen LUMO orbital of Naproxen



HOMO orbital of Paracetamol LUMO orbital of Paracetamol



HOMO orbital of Phenazone LUMO orbital of Phenazone



HOMO orbital of Propylphenazone LUMO orbital of Propylphenazone

HOMO orbital of Ranitidine LUMO orbital of Ranitidine

HOMO orbital of Warfarin LUMO orbital of Warfarin

Figure-1: HOMO and LUMO orbital's of examined medicinal compounds.

The medicinal compound which possessing high E_{HOMO} value has the greater tender to donate rich electrons to the other electron acceptor species (metal). The metal has the empty molecular orbital of low energy which accepts an electron from the electron rich organic compounds. In our investigation, Caffeine (E_{HOMO}: -10.79), Naproxen (E_{HOMO}: -10.31), Phenazone (E_{HOMO}: -10.11), Propylphenazone (E_{HOMO}: -9.855), and Ibuprofen (E_{HOMO}: -9.703) exhibits highest values of E_{HOMO} in e V. These compounds expected to adsorb chemically or physically on the surface of electrode (metal) in order to block the dissolution or disintegration process. The electron rich elements in these compounds are expected to play major role in the corrosion inhibition property. The nature of reactivity of organic compound on the metal surface can be explained by based on energy gap values. As the energy gap value decreases, then reactivity of organic compound on the surface of the metal increases which enhances the protection efficiency of the medicinal compound. Smaller energy gap values will cause to be superior protection efficiencies because energy to take out an electron from final occupied orbital will be lowered.

Table-2: Quantum chemical parameters (by using PM3 method)

Name of medicinal compound	E_{HOMO} (eV)	E_{LUMO} (eV)	Energy gap (eV)	I	A	η	χ	σ	μ	ω
Acetaminophen	-3.499	3.974	7.474	3.499	-3.974	3.736	-0.237	0.267	0.237	0.00751
Aspirin	-9.580	-3.240	6.340	9.580	3.240	3.170	6.410	0.315	-6.410	6.48075
Caffeine	-10.79	-3.455	7.337	10.792	3.455	3.6685	7.123	0.272	-7.120	6.909
Ibuprofen	-9.703	-2.857	6.846	9.703	2.857	3.423	6.28	0.292	-6.280	5.760
Naproxen	-10.31	-2.367	7.945	10.312	2.367	3.972	6.339	0.251	-6.339	5.058
Paracetamol	-3.499	3.972	7.471	3.499	-3.972	3.735	-0.236	0.267	0.236	0.00748
Phenazone	-10.11	-2.965	7.154	10.119	2.965	3.577	6.542	0.279	-6.542	5.990
Propylphenazone	-9.855	-3.945	5.91	9.885	3.945	2.955	6.900	0.338	-6.90	8.0558
Ranitidine	-9.581	-2.770	6.811	9.5814	2.770	3.4057	6.1757	0.293	-6.175	5.607
Warfarin	-8.977	-2.809	6.168	8.977	2.809	3.084	5.893	0.324	-5.893	5.6301

The reactivity order (based on energy gap concept) follows the following order, Propylphenazone > Warfarin > Aspirin > Ranitidine > Ibuprofen > Phenazone > Caffeine > Paracetamol > Acetaminophen > Naproxen.

Based on the energy gap values, Propylphenazone expected to show that highest corrosion inhibition property on the surface of industrial metals due to high reactivity of this compound compared to the other medicinal compounds. Propylphenazone contains two nitrogen atoms, one oxygen atom and five double bonds, which would like to interact robustly with electrode (metal) surface in corrosive ions acts as superior corrosion inhibition property.

High I values show the chemical inertness and high stability of the organic compound. The low I values show the high reactivity of the medicinal compound. Low I values hints the good protection efficiency.

Based on the I values, the order of reactivity of the medicinal compounds as follows, Paracetamol > Acetaminophen> Warfarin > Aspirin > Ranitidine > Propylphenazone > Propylphenazone > Phenazone > Naproxen > Caffeine.

Softness and hardness are vital parameters in order to the measurement the reactivity and stability of the medicinal compounds. Propylphenazone has the lowest hardness value (2.955) and 2nd highest softness value when compared to other medicinal compounds. Generally, the organic compound with low hardness and high softness value exhibits the good inhibition property on metal surfaces in concentrated corrosive solutions. Electrophilicity values provide information about the electrophilic or nucleophilic nature of the medicinal compound. High ω values suggest that, the medicinal compound act as a strong electrophile and low ω value shows that, the molecule act as strong nucleophile. Propylphenazone has the highest electrophilicity value indicating that, it acts as electrophile and Paracetamol has the lowest electrophilicity value showing that, it acts as strong nucleophile (Table-2).

Conclusion

E_{HOMO} value obtained from Quantum chemical method shows that, among the examined compounds, Caffeine, Naproxen, Phenazone, Propylphenazone and Ibuprofen molecules strongly adsorb on the metal surface. Based on energy values, Propylphenazone expected to robust anticorrosive property due to their high reactivity. Hardness and softness parameters also strongly support the superior corrosion inhibition of Propylphenazone. The results of quantum chemical studies indicate that, all the examined medicinal compounds exhibits anticorrosion property with variation in the protection efficiency. These results give strong plot form to experimental investigation of corrosion inhibitors in order solve metal dissolution process.

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